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Chiroptical Molecular Memory of Amorphous Azopolymer using Light Handedness

Mi Jeong Kim and Dong-Yu Kim
Department of Materials Science and Engineering,
Kwang-Ju Institute of Science and Technology, Kwangju, 500-712, KOREA.

ABSTRACT

For chirooptic molecular memory system, induced chirality on an azobenzene-containing amorphous polymer film was investigated using circularly polarized Ar+ laser with various ellipticity. High intense CD spectrum proved that optical-induced chirality on the amorphous film. Additionally, elliptically polarized light induced much higher chirality than circularly polarized light.

INTRODUCTION

Molecular optical switches, which can interchange between two distinct states by exposing it to light with different wavelengths or polarization, are expected to play an important role in various novel organic optical devices. Many researchers have investigated photochemical compounds, which can interchange between two conformational isomers by selective isomerization reaction upon irradiation at two different wavelengths. Azobenzenes, diarylethenes, flugides, spiropyrans are a few examples [1]. However, most of these photochromic compounds suffer from poor temporal stability and fatigue resistance due to different energy states of two isomers. Another advantage of chirooptical switching is possible non-destructive readout capability by reading the signal outside of absorption band.

Chiral materials are good candidates for these purposes due to two distinct bistable structures with the same energy and non-centrosymmertic properties in both molecular and macroscopic levels. Only difference of stereoisomers is optical rotation in opposite direction. In order to realizing reversible optical data storage systems, proper chiral structures must be designed to exhibit *switchable chirality*, which means two enatiomers are reversibly interchangeable by optical means. Recently, helical shaped molecules were focused for chirooptic molecular memory systems because their two enatiomers with opposite direction helicity can be interchanged by exposing it to circularly polarized light [1].

Azobenzene containing polymers are widely known photochromic materials due to alignment tendency to perpendicular direction of incident light polarization through trans-cis-trans photoisomerization cycles. Photo-induced chirality using circularly polarized light has been reported in azobenzene liquid crystalline polymers [2, 3]. However, for azobenzene-containing amorphous polymers, chirality induction and switching capability using circularly polarized light is not clear at present. The object of this research is to investigate chirooptical induction and memory of azobenzene-containing amorphous polymers without chiral carbon center when its solid film is exposed to various states of circularly polarized light.

EXPERIMENTAL

Epoxy based azobenzene amorphous polymer without chiral carbon center (PDO3) was synthesized as previously reported [4] and the chemical structure is shown in Figure 1. Glass transition temperature (T_g) and thermal stability of PDO3 were measured using differential scanning calorimeter and thermogravimetric analysis (TA Instrument). Substrate for the solid film was glass slide, which was cleaned by sonication in surfactant solution, acetone and water. Optically transparent films were prepared by spin casting process using 10wt% cyclohexanone solution and were baked at 160°C during overnight. The film thickness was 0.48 μm measured by α-step instrument.

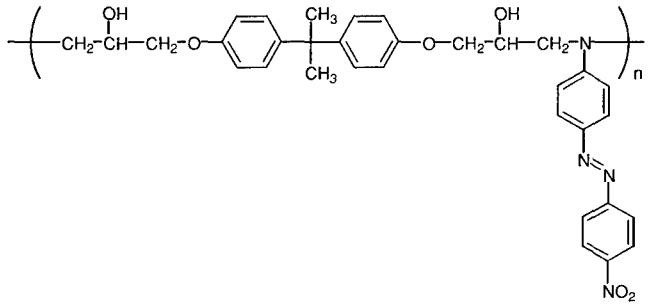

Figure 1. The chemical structure of epoxy based azobenzene amorphous polymer PDO3.

An Ar^+ ion laser beam (Coherent INNOVA skylight 305C) at a wavelength of 488 nm was used as a light source for chirality induction. The intensity of the expanded beam was 160 mW/cm^2. Ellipticity and handedness of circular polarization were controlled using a λ/4 waveplate and the beam profiles were measured using a linear polarizer before and after irradiation on the azobenzene polymer film. All exposure time was fixed to 10 min. Circular dichroism (CD) spectra of irradiated films as a function of ellipticity of incident light were measured using JASCO 720 instrument.

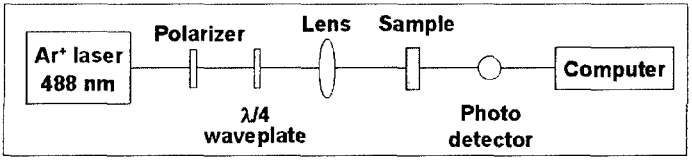

Figure 2. Optical set-up for chirality induction on the polymer film

RESULTS AND DISCUSSION

In order to investigate photo-induction of chirality on azobenzene containing amorphous polymer solid film, we synthesized PDO3 as shown in Figure 1. PDO3 polymer exhibited glass transition at 110°C and were thermally stable up to 266°C with 5% weight loss. The solid film obtained by spin coating was highly transparent due to amorphous properties of the material. The absorption maximum was at 456 nm measured by UV spectroscopy. The polymer films did not show any circular dichroism before irradiation. This was expected from the fact that the polymer structure is achiral.

Figure 3 shows CD spectra results of PDO3 polymer films after irradiation. When the PDO3 films were exposed to circularly polarized light (R-CLP or L-CPL), induced circular dichroism was negligible. However, in the case of elliptically polarized light, much larger CD on the film was induced. The CD spectra of the PDO3 films exposed to right and left-handed elliptically polarized light showed almost symmetric mirror images, which means that two different enatiomeric structures were produced by irradiation with opposite handedness.

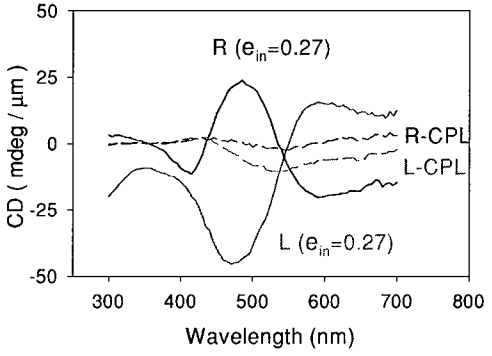

Figure 3. CD spectra of PDO3 films after exposed to circularly right and left polarized light (R-CLP and L-CPL), and elliptically polarized light (e_{in} = 0.27) during 10 min. e_{in} designate the ellipticity of incident radiation.

Figure 4 shows that the induced CD signal is strongly dependant on the ellipticity of the incident light, which is varying from linear polarization to circular polarization. Irradiation of the laser beam with linear polarization (e_{in} = 0) was not efficient to induce chirality on the azobenzene amorphous polymer PDO3 film. In the case of polarized light with small ellipticity (e_{in} = 0.05), the intensity of induced CD was –190 mdeg/μm at 415 nm. As the ellipticity of the beam increased further, the induced CD became smaller, and when the beam profile approached to circularly polarization state, the CD signal became negligible again. Even though dependence of ellipticity on optical rotation was reported [5], this kind of strong dependence of ellipticity on induced circular dichroism has never been reported before. We are currently investigating the detailed mechanism of this process and the nature of the induced CD.

Induced CD signal remained after several days with slightly reduction of the intensity. Therefore, the photo-induced chirality on the amorphous solid film of azobenzene polymer was believed to be due to permanent change of molecular conformation not due to temporary cis isomer population.

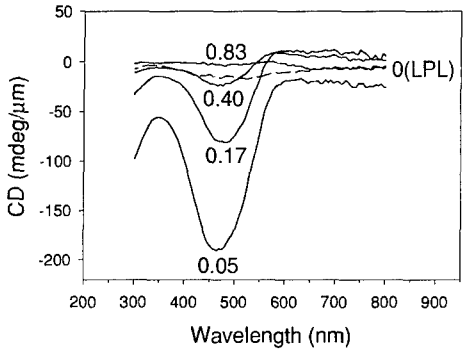

Figure 4. CD spectra of PDO3 films after exposed to left-handed circularly polarized light with different ellipticity during 10 min. The numbers represent the ellipticity of incident radiation in each case.

CONCLUSIONS

In this report, we have clearly shown that chirality can be optically induced in amorphous azobenzene-containing polymer film from measurement of CD spectrum. Elliptically polarized light induced higher circular dichroism on the film than circularly polarized light. It has been argued that highly organized structures such as LC phases may be responsible for this process. However, we have shown, from our experiments, liquid crystalline phase is not necessary to observe optically induced circular dichroism in azo-polymers. Further exploration of this process may open up a novel approach for the bistable chirooptical data storage applications.

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REFERENCES

1. B. L. Feringa, R. A. van Delden, N. Koumura and E. M. Geertsema, *Chem. Rev.* **100**, 1789 (2000).
2. L. Nikolova, T. Todorov, M. Ivanov, F. Andruzzi, S. Hvilsted and P. S. Ramanujam, *Optical Materials* **8**, 255 (1997).
3. G. Iftime, F. L. Labarthet, A. Natansohn and P. Rochon, *J. Am. Chem. Soc.* **122**, 12646 (2000).
4. D. Y. Kim, L. Li, X. L. Jiang, V. Shivshanker, J. Kumar, S. K. Tripathy, *Macromolecules* **28**, 8835 (1995).
5. L. Nikolova, L. Nedelchev, T. Todorov, Tz. Petrova, N. Tomova, V. Dragostinova, P. S. Ramanujam and S. Hvilsted, *Appl. Phys. Lett.* **77**, 657 (2000).